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SOURCE Priroda, Vol XLII, No 2, pp 88-92.USSR WORK ON ELECTRONIC PHENOMENA IN CATALYSIS AND ADSORPTION

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[Numbers in parentheses refer to appended bibliography.]

With the discovery of reaction accelerators, or so-called catalysts, industry was given a new means of controlling chemical processes. At present, a whole series of technological processes is based on the action of catalysts, e.g., the manufacture of sulfuric and nitric acids, the synthesis of ammonia, the hydrogenation of vegetable oils, the manufacture of synthetic rubber, the production of synthetic liquid fuel, the cracking of petroleum, etc.

Our native scientists have taken a prominent part in developing scientific conceptions of catalysis, and in creating various branches of chemical industry based on catalysis. In 1811, K. Kirkgof, the Russian academician, discovered the conversion of starch to sugar (glucose) during boiling with dilute sulfuric acid as a catalyst. The catalytic saccharination of starch served as a basis for the creation of the starch-molasses industry, and is a classical example, technically, of an important catalytic reaction which has retained its value.

The works of Aleksandr Mikhaylovich Butlerov played a great part in the development of organic catalysis. His investigations in the field of the catalytic polymerization of hydrocarbons, continued in the works of I. L. Kondakov, A. Ye. Favorskiy, and other scientists, were climaxed in the Soviet period by S. V. Lebedev's creation of a method for obtaining synthetic rubber catalytically.

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Russian scientists discovered and improved catalysts for the processes of addition and removal of hydrogen. This led to the emergence of catalytic methods for the conversion of petroleum. Research in this field, begun by G. G. Gustavson, V. V. Markovnikov, and other scientists, was brilliantly developed by Academician N. D. Zelinskiy and his students.

Thus, it is no exaggeration to say that the most extensive branches of chemical industry arose as a result of the fruitful investigations of native chemists in the field of catalysis.

Our native scientists performed services no less important in developing the theory of catalysis. Dmitriy Ivanovich Mendeleev, the author of the periodic law of the elements, made a number of statements regarding the role of the catalyst and its effect on the chemical processes. In his article, "Memorandum on the Effect of Contact on the Course of Chemical Conversions," written in 1886 and devoted to the questions of the theory of catalysis and catalytic effects, Mendeleev dwells in detail on the interaction of molecules of reacting substances with the surface atoms of an active solid body [of a catalyst], and pays particular attention to the deformation of the molecules of the reacting substances which takes place on the surface of the catalyst, a deformation which increases the reacting capability of the molecules.

N. D. Zelinskiy expanded the ideas of Mendeleev concerning the deformation of molecules on the surface of a solid catalyst. His works were based on the theory which postulated that, for the catalyst's action to be effective, and for deformation of the reacting molecules on the catalyst's surface to be attained, it was necessary that the distance between the active centers of the catalyst correspond to the distance between the atoms in the molecule of the reacting substance.

A new trend in the study of the mechanism of catalytic processes which take place in the presence of solid catalysts was developed by Academician L. V. Pissarzhevskiy in 1926 - 1934. He demonstrated for the first time the role which free electrons in solids play during catalytic processes.

Pissarzhevskiy (1) assumed that the ability of the catalyst to speed up the chemical processes was linked to the possibility of the transfer of electrons from the catalyst to the reacting molecules. Hence, it follows that those substances which have a great number of free electrons must be particularly active in relation to chemical processes involving transfer of electrons (primarily as far as the processes of oxidation and reduction are concerned). Such substances are the so-called transition metals: manganese, nickel, cobalt, and others, and some of their compounds (oxides, sulfides, etc.).

Pissarzhevskiy and his collaborators determined, in particular, that the rate of decomposition of hydrogen peroxide in the presence of manganese dioxide is greater than in the presence of lead dioxide. This they explained by pointing out that manganese belongs to a type of metal which has incomplete groups in electronic shells, whereas lead does not belong to this type.

Assuming that illumination with ultraviolet light would facilitate the escape of electrons from a catalyst, Pissarzhevskiy and his collaborators studied the combined action of radiation and of the catalyst. For this purpose, they filled two quartz vessels with a detonating  $H_2 - O_2$  mixture (a mixture of two parts of hydrogen and one part of oxygen) and at the same time placed a platinum foil in one of the vessels to serve as a catalyst. The radiation of a quartz mercury-vapor lamp was alternately directed at both vessels. During this irradiation, there were no visible changes observed in the vessel without platinum; but as soon as the radiation was directed at the vessel containing the platinum, an explosion was heard, and the walls of the vessel were covered with

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a film of almost imperceptible droplets of water. Consequently, the catalytic activity of platinum was abruptly increased as a result of exposure to ultra-violet light. Analogous experiments were also conducted relative to the catalytic decomposition of hydrogen peroxide.

The ideas of Pissarzhevskiy, naturally, were tied to that conception of the atom and those notions of the structure of a solid body which were prevalent during 1913 - 1925, and from which contemporary physicists have departed. In certain works, for example, the part played in catalytic processes by the mechanical impact of electrons was overrated. But it must be noted that the basic ideas of Pissarzhevskiy concerning the role of the electronic structure of solid bodies and of electronic transitions in catalytic processes, when translated into the language of contemporary physics, have retained their value.

Today, the concepts concerning the electronic character of the processes of catalysis and adsorption are being developed in the works of S. Z. Roginskiy, Corresponding Member of the Academy of Sciences USSR, and of Prof F. F. Vol'kenshteyn. (2)

From the standpoint of these concepts, solid bodies, which play a fundamental role in catalysis, can be divided because of their electronic properties, into two groups, namely, metallic crystals with an atomic lattice (see Figure 1a) [figures are appended] and crystals with an ionic lattice consisting of positively and negatively charged ions (see Figure 1b). Bodies with other lattices are of secondary importance as far as catalytic activity is concerned. According to contemporary notions, electrons of a solid body possess a distinct energy. Figure 2 shows the relative position of energy levels in a dielectric, a semiconductor, and a conductor (metal). The filled electrons levels, i.e., levels consisting of electrons securely bound to a lattice of a solid body, are represented by a double crosshatch, whereas levels of free electrons or levels of conductivity are represented by a single crosshatch. Conductivity electrons move freely along the entire crystal and serve as carriers of the electric current. Furthermore, in the crystals there are so-called surface levels which form a surface zone of conductivity.

Electrons which correspond to these levels can move freely along the surface of the crystal, but cannot freely withdraw from it into the body of the solid. These are the electrons which are essential for catalysis.

Metals, by their properties, are sharply differentiated from semiconductors and dielectrics. Actually, electrons of a metal can easily pass over from a lower filled level to free levels. On the contrary, to pass over from filled levels to free levels, electrons in a semiconductor have to obtain an additional energy  $E$  (see Figure 2), for example, light energy or heat energy. A still greater energy has to be expended to transfer electrons from a lower zone to a zone of conductivity in a dielectric (insulator).

Certain semiconductors can acquire a marked conductivity at room temperature. In contrast to this, insulators do not conduct current even at fairly high temperatures. Most catalysts, particularly many oxides, salts, and other compounds, are semiconductors. Some of these are distinguished by a specific color. This testifies to the occurrence of electronic processes in connection with chemical reactions that take place on the crystal surface.

The research of S. Z. Roginskiy, S. Yu. Yelovin, G. M. Zhabrova, and L. Ya. Margolis (3) on the reactions of the complete oxidation of hydrocarbons determined that the greater the intensity of the color of the catalysts, the greater the catalytic activity which distinguishes them.

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The connection between color and catalytic activity was observed (according to published data) also in regard to processes involving the addition of hydrogen, i.e., hydrogenation, and the splitting off of hydrogen, i.e., dehydrogenation. At the same time, there are a great number of reactions, for example, the reactions of isomerization, cracking, hydrolysis, and others, which take place at a fast rate on colorless compounds.

S. Z. Roginskiy suggested a classification of catalysts and catalytic processes on the basis of the observed laws of catalytic transformation and of the chemistry of catalytic processes. According to this classification, the fundamental catalytic processes can be divided into two major classes.

Those processes associated with the transfer of electrons belong to the first class -- oxidation, hydrogenation, and dehydrogenation. Typical catalysts for these processes are substances which have free electrons, or electrons which pass over easily to the free state. Electronic transitions play an essential role in the mechanism of catalytic processes of this type.

Those reactions not associated with the transfer of electrons belong to the second class, as for example, reactions of cracking, isomerization, esterification, dehydration, and others. An entire range of electronic properties of catalysts has no influence on this category of processes. Thus, the color of the catalysts and the presence of transitional elements in them have no significance whatsoever. On the contrary, the ability of the catalysts to transmit protons has great significance. Acids and bases belong to catalysts of this type. During catalysis with acids, the addition of the proton to the reacting substance is one of the stages of the reaction. Therefore, the active catalysts for the second group of processes would be, apart from the liquid inorganic acids, also those solid catalysts which have acid properties, for example, aluminosilicates, on the surface of which ions of hydrogen (protons) are adsorbed. If such a catalyst is treated with an alkali, i.e., if the ions of hydrogen are removed from its surface and replaced with ions of an alkali metal, then the activity of the catalyst is sharply diminished.

The classification of catalysts according to their electronic properties made possible a certain amount of orientation in connection with the selection of catalysts for processes to be applied in industry. The introduction of a definite kind of admixtures ("activators") into the catalysts has a very great effect on their action. These "activators" increase the activity of the catalysts, the selectivity of their action in relation to the requisite reaction, their stability in relation to the temperature effects, etc. These admixtures can fundamentally change the electronic properties of catalysts which are of the semiconductor type.

Numerous experimental investigations by Soviet physicists (for example, Academician A. F. Ioffe, V. Ye. Loshkarev, Active Member of the Academy of Sciences Ukrainian SSR, and others) revealed that an abnormally strong influence on the electronconductivity of semiconductors is exerted by a foreign substance (admixture) which is capable of changing the energy of the electrons, i.e., their energy levels. Such action by an admixture is represented schematically in Figure 3. In this action the admixtures promote the emergence of new energy levels which lessen the energy necessary for the transition of the electron to the zone of conductivity of the semiconductor catalyst. At the same time, the transition of the hole (i.e., a positive charge remaining in place of the electron) to a lower zone is facilitated. (4)

F. F. Vol'kenshteyn (5) analyzed theoretically the dependence of the activity of a semiconductor catalyst on the admixture within it and showed that the effect of the foreign substance on the catalyst's activity is made obvious by the change in the concentration of electrons in the surface layer of the catalyst's lattice. The activity of the catalyst depends on the concentration of the electrons and, consequently, is controlled by the admixture.

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A catalytic reaction in most cases represents a complex process which passes through a whole series of successive stages: the movement of reacting molecules to the surface of the catalyst (diffusion), the adsorption of these molecules on the catalyst, the chemical reaction proper and, finally, the desorption and withdrawal of the products of the reaction from the surface of the catalyst.

Adsorption plays an essential role in this succession of stages. It is necessary to differentiate ordinary physical adsorption, which amounts to almost instantaneous absorption by the surface of the adsorbent or catalyst of molecules of gas, vapor, or liquid, without the consumption of additional energy, from activated adsorption.

Activated adsorption, in contrast to physical adsorption, proceeds more slowly, and its rate exhibits a strong dependence on temperature. In many cases the relationship governing the change in the rate of activated adsorption as a function of time is similar to the relationships which express the rate of chemical processes in the presence of a catalyst. This permits the assumption that the process of activated adsorption of the reacting substances on the surface of a catalyst may be the essential stage of the catalytic process.

The research into the process of activated adsorption by optical methods carried on by Academician A. N. Terenin and his collaborators is very interesting. This research showed that the surface of the adsorbent exerts the strongest influence on adsorbed substances; for example, in certain instances, it produces a coloration in them (6). At the same time, it was established by many researchers that, in a number of cases, the electrical properties of the catalyst were changed during the course of activated adsorption on the catalysts.

All this brought about the need for a theoretical study of the processes of adsorption from the viewpoint of electronic concepts. Let us examine certain laws of adsorption on ionic semiconductors which are based on the theoretical work of F. F. Vol'kenshteyn. In Figure 4, an ionic crystal is schematically represented. This crystal is constructed from single-charge ions. Atom A, with one valence electron, approaches the surface of such a crystal. While atom A is sufficiently far from the surface of the crystal, the valence electron is attached to this atom (a).

During adsorption, when atom A approaches the surface of the catalyst, its electron no longer belongs only to this atom but, strictly speaking, to the whole system in its entirety. Calculation shows that the valence electron of atom A, to a greater or lesser degree, is found to be drawn into the lattice of the catalyst (b). By this drawing in of the electron, a bond is fashioned between the adsorbed atom A and the crystal of the catalyst.

If atom A, falling on the surface of the crystal, meets one of the free electrons traveling in the zone of conductivity, then it is joined with it and activated adsorption (c) takes place. Atom A is attached to the surface and the free electron of the lattice is fixed near the atom. The adsorbed atom plays the part of the "admixture" for the free electron of the lattice, creating a local energy level in which the free electron is captured on removal from the zone of conductivity. This results in the formation of the dielectronic bond (d). Hence, in this case the free electron of the lattice acts as an adsorption center. The more complex adsorption of a molecule, rather than of an atom, on the surface of a crystal has not yet been considered theoretically.

Thus, in agreement with the electronic theory of adsorption developed by Vol'kenshteyn (7), the centers of adsorption possess a number of specific properties. They are not fastened to the crystal, but wander along its surface. As soon as adsorption takes place at such a wandering center, it is fastened to the surface.

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It is possible to change the concentration of free electrons which are centers of adsorption by introducing an admixture into the lattice of the crystal, or by exposure of the crystal's surface to light possessed with such frequency and energy as to transfer the electrons from the normal zone to the surface zone of conductivity.

These new electronic ideas concerning the process of adsorption indicate ways of controlling the process of activated adsorption. But, of course, they require experimental verification. Further work on the electronic theory of adsorption and catalysis must clear up a number of problems the solution of which is necessary for the understanding of the mechanism of catalysis.

## BIBLIOGRAPHY

1. L. V. Pisarzhevskiy, Izbrannyye Trudy, (Selected Works), Publishing House of the Academy of Sciences Ukrainian SSR, Kiev, 1936
2. S. Z. Roginskiy and F. F. Vol'kenshteyn, Elektronnaya Priroda Kontaktnykh Yavleniy, "Kataliz" (Electronic Nature Phenomena, "Catalysis"), Trudy Vsesoyuznogo Soveshchaniya po Katalizu (Works of the All-Union Meeting on Catalysis) Dedicated to the Memory of L. V. Pisarzhevskiy Publishing House of the Ukrainian SSR, Kiev, 1950, pp 9-40
3. S. Z. Roginskiy, S. Yu. Yelovin, G. M. Zhabrova, and L. Ya. Margolis, Doklady Akademii Nauk SSSR, Vol LII, 1946, p 425
4. A. F. Ioffe, Elektronnyye Poluprovodniki (Electronic Semiconductors), State Publishing House for Technical and Theoretical Literature, 1933; "Semiconductors in Contemporary Physics," Priroda, No 12, 1952
5. F. F. Vol'kenshteyn, Zhurnal Fizicheskoy Khimii, Vol XXIV, 1950, p 1068
6. A. I. Sidorova and A. N. Terenin, "The Nature of Spectral Displacement During the Sorption of Aromatic Amines on Active Clays," Izvestiya Akademii Nauk SSSR, Department of Chemical Sciences, No 2, 1950, p 152
7. F. F. Vol'kenshteyn, Zhurnal Fizicheskoy Khimii, Vol XXI, 1947, p 1317; Vol XXVI, 1952, p 1462

[Appended figures follow.]

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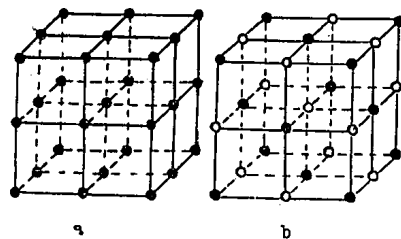


Figure 1. (a) Atomic Lattice of a Crystal of the Conductor Type (Metal); (b) Ionic Lattice of a Crystal of the Semiconductor Type (Sodium Chloride)

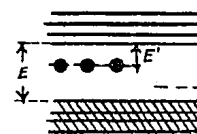


Figure 3. The Emergence of Additional Levels as a Result of the Introduction of Admixtures into an Ionic Lattice



Insulator Semiconductor Conductor

Figure 2. Diagram of the Relative Position of Energy Levels in an Insulator, Semiconductor, and Conductor

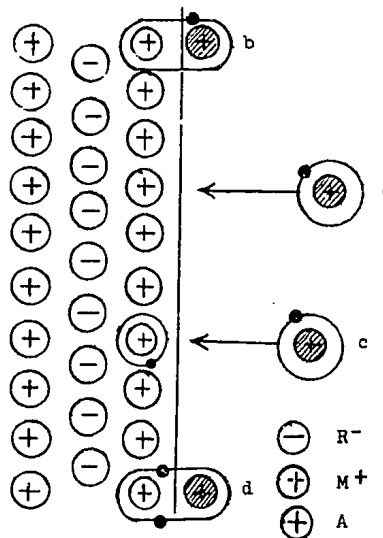


Figure 4. Pattern of the Process of Adsorption on an Ionic Crystal, with the Formation of Mono-electronic and Dielectronic Bonds

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